Quantum Chemistry Problem Set 2
Due: 10:30 am, Monday, 22-Sept.

Note: $\star$ questions are optional and are worth extra credit if correct.

Problem 1 *According to the Bohr-Sommerfield quantization condition, the quantum number of a system is related to the phase-space area enclosed by a periodic path divided by by Planck's constant:*

$$n = \frac{1}{h}\oint p \cdot dx.$$

Using Bohr-Sommerfield quantization, estimate the quantum number for the following systems in a gravitational field, $V(x) = mgx$ using.

$$n = \frac{2}{h}\int_0^X \sqrt{2m(E - mgx)}dx$$

where X is the maximum height of the particle. Hint: if you use Mathematica, compute the intergral

$$\int \sqrt{1 - \beta x}dx$$

first, then apply the limits.

1. *a 1 g piece of chalk 1 m from the floor.*
2. *an electron 1 cm above a reflective surface.*
3. *a 0.0005 g ant 1mm from the floor.*

Problem 2 *Derive an expression for the time-evolution of a free particle.*

$$\psi(x,t) = \int K(x,x',t)\psi(x',0)$$

where $K(x,x',t)$ is the free particle propagator:

$$K(x,x',t) = \langle x|e^{-ih_o t/\hbar}|x'\rangle$$

and h_o is the Hamiltonian for the free particle:

$$h_o = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}.$$

To do so, first show that the eigenstates of h_o are plane-waves

$$\phi = e^{ikx}$$

and write K as a Fourier transform integral.

Problem 3 *Show that the Fourier transform of a gaussian is another gaussian.*

Problem 4 *Compute the uncertainty product* $\Delta x \Delta p$ *for a gaussian wavefunction*

$$\psi(x) = N e^{-x^2/\sigma^2}$$

where N *is the normalization.*

Problem 5 *Plot the uncertainty product for an electron in a 1Å box as a function of quantum number.*

Problem 6 *The Hamiltonian for a particle in a given well is given by*

$$H = \frac{p^2}{2m} + x^2$$

and let $|\phi_n\rangle$ *be an eigenstate solution of*

$$H|\phi_n\rangle = E_n|\phi_n\rangle$$

for $n = 0, 1, \ldots$ *Show by using the commutation relations of* $[x, H]$ *and* $[p, H]$

$$\langle\phi_n|p|\phi_m\rangle = a_{nm}\langle\phi_n|x|\phi_m\rangle$$

where a_{nm} *is some constant. From this, show that*

$$\sum_m (E_n - E_m)^2 |\langle\phi_n|x|\phi_m\rangle|^2 = \frac{\hbar^2}{m^2}\langle\phi_n|p^2|\phi_n\rangle$$

Problem 7 *The ground state energy for a particle in a 3 dimensional box with volume* $V = abc$ *is given by*

$$E = \frac{\hbar^2\pi^2}{2m}\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}\right)$$

Keeping the volume of the box constant, find the dimensions of the box which minimizes the energy. Hint, define a Lagrange multiplier, $\phi = V - abc = 0$ *and take the derivative of* $E(a, b, c) + \phi$ *with respect to each box length, setting each to 0.*

Problem 8 *Compute the commutation relations for the following pairs:*

1. x *and* d/dx
2. x *and* xd/dx
3. p *and* xd/dx
4. $V(x)$ *and* d^2/dx^2

Problem 9 *Compute the Poisson bracket relation between the following pairs:*

1. x *and* p
2. x *and* xp
3. p *and* xp
4. $V(x)$ *and* p^2

Compare these to the results you obtained above in the previous problem.

Problem 10 *In the first problem set, you showed that for a one-dimensional classical system with Hamiltonian*

$$H = \frac{p^2}{2} - \frac{1}{2q^2},$$

$$D = \frac{pq}{2} - Ht$$

is a constant of the motion. Does the same hold true for the quantum mechanical system?